(12) STANDARD PATENT (11) Application No. **AU 2001289724 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Multi-layered coating systems consisting of a thick, gel-type base coat and a top coat of polyurethane lacquer, production and use thereof

(51) International Patent Classification(s)
C08G 18/10 (2006.01) ***C08G 18/78*** (2006.01)
B05D 7/00 (2006.01) ***C09D 5/00*** (2006.01)
C08G 18/48 (2006.01) ***C09D 175/04*** (2006.01)

(21) Application No: **2001289724** (22) Date of Filing: **2001.07.23**

(87) WIPO No: **WO02/10241**

(30) Priority Data

(31) Number	(32) Date	(33) Country
10037157	**2000.07.31**	**DE**

(43) Publication Date: **2002.02.13**
(43) Publication Journal Date: **2002.05.09**
(44) Accepted Journal Date: **2007.05.10**

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(56) Related Art
US4456642

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
7. Februar 2002 (07.02.2002)

PCT

(10) Internationale Veröffentlichungsnummer
WO 02/10241 A1

(51) Internationale Patentklassifikation⁷: **C08G 18/08**, 18/48, C08J 7/04, B05D 7/00

(21) Internationales Aktenzeichen: PCT/EP01/08479

(22) Internationales Anmeldedatum: 23. Juli 2001 (23.07.2001)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
100 37 157.4 31. Juli 2000 (31.07.2000) DE

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(81) Bestimmungsstaaten *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Bestimmungsstaaten *(regional)*: ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:
mit internationalem Recherchenbericht
— *vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen*

(54) Title: MULTI-LAYERED COATING SYSTEMS CONSISTING OF A THICK, GEL-TYPE BASE COAT AND A TOP COAT OF POLYURETHANE LACQUER, PRODUCTION AND USE THEREOF

(54) Bezeichnung: MEHRSCHICHTIGE BESCHICHTUNGSSYSTEME AUS EINER DICKSCHICHTIGEN, GELARTIGEN GRUNDSCHICHT UND EINER DECKSCHICHT AUS POLYURETHAN-LACK, DEREN HERSTELLUNG UND VERWENDUNG

(57) Abstract: The invention relates to a multi-layered coating, consisting of a) a base coat of a high-molecular, gel-type polyurethane and b) a top coat consisting of polyurethane lacquer. The invention also relates to the production and use (application) thereof.

(57) Zusammenfassung: Die Erfindung betrifft eine mehrschichtige Beschichtung, bestehend aus a) einer Grundschicht aus hochmolekularem, gelartigem Polyurethan und b) einer Deckschicht bestehend aus Polyurethan-Lack deren Herstellung und Verwendung (Applikation).

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Mehrschichtige Beschichtungssysteme aus einer dickschichtigen, gelartigen Grundschicht und einer Deckschicht aus Polyurethan-Lack, deren Herstellung und Verwendung

Die Erfindung betrifft ein mehrschichtiges Beschichtungssystem aus einer dickschichtigen, gelartigen Grundschicht und einer Deckschicht aus Polyurethan-Lack, deren Herstellung und Verwendung (Applikation).

In der Automobilindustrie ist heutzutage als Standard für z.B. die Instrumententafel

- ein unbeschichteten Kunststoff zu verwenden (Billig-Lösung mit schlechter Optik und Haptik und schlechten Beständigkeiten gegen Umwelteinflüsse),
- einen Systemaufbau bestehend aus Polyurethanschaum und Folie, Textil oder Leder als Dekorschicht mittels Klebkaschierung zu applizieren (gute Haptik, aber hohe Kosten durch komplizierte Herstellung),
- die eingesetzten Kunststoffe nachträglich zu lackieren, z.B. mit einem 2K-Polyurethan basierenden 50μm dünnen Softfeel Lack (mittlere Haptik, gute Beständigkeiten, mittlerer Preis).

Dies gilt im übertragenen Sinne auch für die anderen Einsatzgebiete von Kunststoffen, die im direkten Kontakt mit der menschlichen Haut stehen. Der Softeffekt der dünnen Softfeel-Lackschichten lässt sich nur in Grenzen vergrößern (z.B. durch Erhöhung der Schichtstärke auf 100μm), wobei die Beständigkeiten und die Optik des Lackfilms meistens schlechter werden.

Auch der Systemaufbau Träger/Schaum/Folie hat etliche Nachteile:

- Der Herstellaufwand ist hoch, daher sind diese Systeme teuer.

Multi-layered coating systems consisting of a thick gel-type base coat and a top coat of polyurethane lacquer, production and use thereof

The present invention relates to a multilayer coating system comprising a thick, gel-like base layer and a top layer of polyurethane lacquer, and their production and use (application).

In the automobile industry it is nowadays standard practice for e.g. the instrument panel

- to use an uncoated plastics material (cheap solution with poor optical and haptic properties and poor resistance to environmental influences),

- to apply a composite structure consisting of polyurethane foam and film, textile material or leather as decorative layer by means of adhesive bonding (good haptic properties, but high costs due to complicated production),

- subsequently to lacquer the employed plastics materials, e.g. using a two-component polyurethane-based 50 μm thin soft-feel lacquer (average haptic properties, good resistance properties, average price).

This also applies as appropriate to the other areas of use of plastics materials that come into direct contact with human skin. The soft effect of the thin soft-feel lacquer layers can be enhanced only within certain limits (e.g. by increasing the layer thickness to 100 μm), and moreover the resistance properties and optical properties of the lacquer film are generally impaired.

The composite structure consisting of carrier/foam/film also has a number of disadvantages:

- The production costs are high and accordingly such systems are expensive.

- The light-fastness is often not adequate.
- The use of plasticisers in the films contributes significantly to fogging.

Anhydrous gel compositions such as are described for example in EP-A 0 057 838 and EP-A 0 057 839 have in the meantime become widely available on the market and are manufactured and used according to the processes described in these publications. These applications relate to anhydrous gel compositions, gel compositions with a depôt effect optionally containing active substances, consisting of a polyurethane matrix and high molecular weight polyols as dispersing agents and optionally active substances, as well as to a process for the production of the gel compositions, optionally in the presence of the active substances. Biocides, pharmaceuticals, ethereal oils, fragrances, colouring agents, cleaning agents, anti-ageing agents, lubricants and antistatics, and other materials may be used as active substances. The gel compositions may be employed as casting or pouring compositions or as mouldings containing active substances having a depôt effect of the said active substances. These gels are of course used as such and are covered with for example films or textile materials in order to permit use as a block gel.

Water-based gels have been used for some years in many technical sectors (see for example R.L. Whistler, Industrial Gums, Academic Press, InC., New York, 1973 and DE-A 2 347 299). A particularly interesting property of the gels is that they possess a high casting accuracy. This is utilised in order to duplicate mouldings. In this case the body to be cast is recast with the gel-forming composition. The moulding is removed after the gel formation. A gel mould is obtained whose cavity corresponds to the volume of the moulding. An agar-gel is used as duplicating composition, for example in the dental sector. Such compositions have a number of disadvantages however:

a) the gelling takes a long time and has to be carried out under specific process conditions,

b) the elasticity of the gel is not sufficiently high for the demoulding of thin crosspieces and undercuts,

c) the dimensional stability is unsatisfactory, and

d) if the gel mould is kept in the open air the dimensions change even after a very short time as a result of evaporation of water.

Anhydrous casting compositions are also known, for example based on silicone. These are produced by mixing a prepolymer with a small amount of crosslinking agent. The model to be cast is poured together with this reaction mixture and removed after the mixture has hardened. A mould is obtained having a cavity in which castings of the model can then be produced. Anhydrous casting compositions have the following disadvantages however:

a) too high a viscosity for the casting of very fine depressions and undercuts in the surface of the model, and

b) too long reaction times: with the reduction of the reaction time by increasing the proportion of the crosslinking agent the result is an excessive shrinkage of the mould.

Gel compositions containing active substances with a depôt effect, in which the active substances are released to the surrounding medium over a period of weeks to months, are known for example from US-A 3 822 238 and 3 975 350. Furthermore, it is known from DE-A 25 21 265 that water-containing and/or alcohol-containing polyurethane-polyurea gels can be produced in the presence of fragrances. Carrier materials based on water-containing gels are described, which may contain a very wide variety of agents, e.g. pharmaceuticals, biocides or fragrances. Such water-based gels have the disadvantage however that many agents, for example biocides, may be relatively rapidly decomposed due to the presence of the water and thus the time of effectiveness of these gels, i.e. the depôt effect, is greatly reduced. It is also known to incorporate solid and/or foamed high molecular weight polyurethanes as active substances (CH-A 289 915).

Such high molecular weight polyurethanes have the disadvantage however that a large proportion of the incorporated liquid agents remains in the polyurethane as a result of the universally high molecular weight structure and/or too high a proportion of rigid material, and are thus lost for the depôt effect. Solid active agents can be used only to a very limited extent; non-volatile solid substances do not migrate out and highly volatile solid substances can diffuse out only for a very short time and in very small amounts.

EP-A 0 057 838 and EP-A 57 839 describe gels based on polyols that have a high casting accuracy without suffering from the aforementioned disadvantages. These gels are obtained by reacting one or more higher functional, high molecular weight polyols in the presence of catalysts and optionally fillers and additives with such an amount of organic diisocyanates and/or polyisocyanates that an isocyanate index of about 15 – 60 is obtained. The term “isocyanate index” denotes the equivalence ratio (NCO/OH) x 100. As has been found, elastic gels according to the invention that are synthesised from a covalently crosslinked polyurethane matrix and one or more polyols rigidly bound therein (i.e. without the danger of an interfering exudation) are obtained only if the isocyanate and polyol components reacting with one another have a certain minimum functionality and if the polyol or polyols are substantially free from fractions with an OH number of more than 112 or have a molecular weight below 800, preferably below 1000.

It was then also found that gel compositions with improved depôt effect, uniform release of active substances, high active substance concentrations, good stability of the active substance additives and good migration ability of the active substances are obtained if active substances are dissolved or dispersed, as additives, in high molecular weight polyols in the polyurethane-forming reaction, and diisocyanates and/or polyisocyanates as well as catalysts and optionally conventional additives are mixed in.

The advantages of these gel compositions is that a high proportion of high molecular weight polyols is present in the only partially crosslinked polyurethane matrix, which permits and regulates the migration and release of the active substances to the outside.

The disadvantage however is the surface of these gels, which is too rubbery and therefore sensitive to dirt, and does not have a good feel (is too tacky) and accordingly has unsatisfactory haptic properties. Either a film or textile material is therefore applied as protective layer. The films are for example also necessary in order to be able to handle the gel at all. This is firstly expensive and furthermore permits only a restricted use, or even no use at all of the gel in various applications where this film interferes (for example the central console in automobile interiors).

A lacquering with an elastic network would be an alternative in this case. It is known to coat for example plastics substrates produced by injection moulding with two-component, conventional (solvent-containing or aqueous) clear lacquers or topcoat lacquers in a spray process. In this way a surface protection can already be achieved with a 10-100 µm thin coating. The elasticity of the coating is matched to that of the substrate and is generally in the range <100%. In this connection a distinction should be made between the bending elasticity, which normally specifies the vertical deformability, and the elongation at break, which specifies the horizontal deformability. With the elongation at break the rebound behaviour after deformation should also be given, which indicates whether a plastic or elastic deformation has occurred. Plastics lacquers or the even harder metallic lacquers do not normally exhibit this behaviour.

In contrast to the lacquering of metal parts, for coating plastics substrates flexible lacquers are used since for example hard lacquers would lead to an embrittlement of the overall structure (plastics material + lacquer). This could result, for example at low temperatures, in a shattering of the structural part due to crack propagation in the event of a mechanical contact. Elastic plastics lacquers thus generally have elongations at break of ca. 5-100% and may be loaded in the bending test (bending of a lacquered Bayflex substrate) down to –20°C without undergoing crack formation. The rebound behaviour is however in most cases only moderate, since the lacquer has formed a solid polymer network. Also, thermoplastics materials for example generally have a <5% rebound behaviour. However, elastic substrates such as solid gels for example still exhibit an intact rebound behaviour to the original state even at considerably higher elongation at break values (in some cases >1000%).

In order to protect the surface of gels as indicated above, for example against dirt, scratching, light influences and weathering, as well as against solvents, a lacquering would be appropriate. However, the typical elastic plastics lacquers are inadequate, especially as regards two aspects:

- the adhesion to such elastic substrates capable of recovery (even after weathering) is unsatisfactory;

- the elongation at break and rebound behaviour of elastic substrates is adversely affected by an insufficiently elastic lacquer layer (for example the whole gel can crack or the lacquer can flake off).

With gels there is also the additional requirement that in many applications the surface should have haptic properties (bicycle saddles, seat cushions, etc.), and at the same time must also be resistant to solvents, chemicals (acids, alkalis, detergents) and to weathering. This requirement cannot be met with conventional coatings. For example, the Impranil® C solution described in EP-A 057 839 is unsatisfactory as a coating since it does not have adequate resistance to solvents.

The present invention seeks to provide coating systems that do not exhibit the aforementioned disadvantages and which moreover offer advantages as regards handling and haptic properties (gripping behaviour on the surface).

It has now surprisingly been found that in a combination structure consisting of a base layer formed from a high molecular weight, gel-like polyurethane and a top layer of polyurethane lacquer, an overall coating can be obtained that has the desired properties:

- high horizontal haptic properties due to the gel-like base layer,
- high vertical haptic properties due to the top layer of polyurethane lacquer,
- good resistance to environmental influences imparted by the top layer,
- high expansibility and at the same time high rebound behaviour after both layers have been subjected to pressure and/or tensile stresses.

The present invention relates to a multilayer coating comprising

a) a base layer of high molecular weight, gel-like polyurethanes,

b) a top layer consisting of polyurethane lacquer

which can be applied to any suitable substrates and can be used in all areas of industrial application where a surface is to be produced that is characterised by

- outstanding soft effect

- and good resistance to environmental influences

- and/or simple production and processing

- and high expansibility and rebound capacity (in order to be able to adapt the mechanical properties ideally to all substrates)

and that does not have the aforementioned disadvantages, as well as its production and use.

It has furthermore surprisingly been found that the advantages of the gels described in EP-A 0 057 838 and 0 057 839 are not affected by this composite structure but are even improved. The composite structure consisting of gel-like polyurethane + top layer thus also exhibits all the advantages of the known gels (EP-A 005 739 and EP-A 005 738).

Besides this, there are however a whole number of further advantages:

- The gel no longer has to be coated with a film or with a textile material, but is lacquered subsequently or preferably directly in the mould and can then be applied jointly with the thick-layer gel composition to other substrates.

- This permits the production of structural parts in one workstage.

- The surface properties are significantly improved (haptic properties, resistances, freedom from dust). The handling is thereby also significantly improved.

- Optical effects (specific single shades, metallic colours or high gloss) can be achieved. This was not possible with the previous combination.

- Also a completely new use is possible, namely the application of the gel-like polyurethane primer to any suitable substrates by knife coating, spraying, pouring, followed by sealing of the surface by the polyurethane lacquering.

- Similarly novel is then also a sandwich combination consisting of polyurethane lacquer/gel-like primer/polyurethane lacquer. This enables for example films to be produced that are provided on both sides with a surface coating. Further composite structures are also possible (for example polyurethane top layer/polyurethane primer/carrier material/polyurethane primer/polyurethane top layer).

The present invention accordingly relates to

a) the production and formation of gel-like base layers comparable to EP-A 0 057 838 in a layer thickness of 0.01-100 mm in combination with

b) a polyurethane protective layer in a layer thickness of 0.005-2 mm of solvent-free, solvent-containing or aqueous, highly elastic polyurethane coatings. The coatings according to the invention exhibit good elongation and rebound behaviour.

The present invention accordingly provides coating systems of

I) anhydrous, gel-like, high molecular weight polyurethane compositions, optionally containing active substances, comprising

(1) 15-62 wt.%, preferably 20-57 wt.%, particularly preferably 25-47 wt.%, referred to the sum of (1) and (2), of a high molecular weight matrix, and

(2) 85-38 wt.%, preferably 80-43 wt.%, particularly preferably 75-53 wt.%, referred to the sum of (1) and (2), of a liquid dispersing agent firmly bound in the matrix by secondary valence bonds, as well as optionally

(3) 0.1-100 wt.%, referred to the sum of (1) and (2), of fillers and/or additives, as well as optionally catalysts for the polyurethane-forming reaction,

wherein

a) the high molecular weight matrix is a covalently crosslinked polyurethane and

b) the liquid dispersing agent consists of one or more polyhydroxyl compounds with a molecular weight between 1000 and 12000, preferably between 1700 and 6000, and an OH number between 20 and 112, preferably between 28 and 84, particularly preferably between 30 and 56, wherein the dispersing agent substantially contains no hydroxyl compounds with a molecular weight below 800, preferably none with a molecular weight below 1000, and

c) optionally 0.1 to 50 wt.%, preferably 0.5 to 35 wt.%, particularly preferably 0.75 to 25 wt.%, of active substances are contained as additives in the gel composition containing active substances, and

II) solvent-containing, solvent-free and/or aqueous polyurethane top lacquers based on

a) polyurethane adducts in a proportion of 0 to 100 wt.%, referred to the total formulation of the top lacquer,

b) flexible polyols with a Tg of –100 to 70°C and an OH content of 0 to 25 wt.% in a proportion of 0 to 90 wt.% of the formulation of the top lacquer,

c) polyisocyanates with a NCO content of 4 to 50 wt.% in a proportion of 0 to 60 wt.% referred to the formulation, as top lacquer, as well as

d) further fillers and auxiliary substances.

Preferred are gels containing 20 to 57 wt.% of the high molecular weight matrix (1) and 80 to 43 wt.% of the liquid dispersing agent (2). The high molecular weight matrix is according to the invention a reaction product of one or more polyisocyanates and one or more polyhydroxyl compounds and one or more polyhydroxyl compounds with a molecular weight between 1000 and 12000 and an OH number between 20 and 112, the mathematical product of the NCO functionality of the polyisocyanates and OH functionality of the polyhydroxyl compounds being at least 5.2.

The coating systems according to the invention preferably comprise 20 to 57 wt.% of the high molecular weight matrix and 80 to 43 wt.% of the liquid dispersing agent, the high molecular weight matrix being a reaction product of one or more polyisocyanates and one or more polyhydroxyl compounds with a molecular weight between 1000 and 12000 and an OH number between 20 and 112, the mathematical product of the NCO functionality of the polyisocyanates and OH functionality of the polyhydroxyl compounds being at least 5.2.

The dispersing agent used according to the invention preferably comprises one or more polyhydroxyl compounds with a molecular weight of 1700 to 6000 and an OH number of 28 to 84.

The coating agents according to the invention are preferably based on flexible polyols with a Tg of –100 to 25°C and a OH content of 0 to 25 wt.%, and are preferably crosslinked with polyisocyanates with an NCO content of 4 to 50 wt.%.

In order to improve the resistance to chemicals, polyisocyanates with an NCO content of 4-50 wt.% may optionally be added in amounts of up to 40% of the total formulation, to the coating systems according to the invention.

Mixing the polyhydroxyl compounds with for example polyacrylates in order to improve the resistance to chemicals is also possible according to the invention.

The top lacquers of the coating system according to the invention are for example formulations of polyurethane top lacquers with

- up to 150% of fillers (e.g. titanium dioxide)
- up to 10% of catalyst (such as DBTL)
- up to 20% of active substances (such as biocides and fragrances)
- up to 10% of additives (such as flow control agents)

- up to 5% of light stabilisers (such as Tinuvin® 1130), as well as

- optionally dyes, pigments, metal glitter etc.

The coating systems according to the invention are suitable for example for producing a multilayer coating comprising

- a gel-like primer with a layer thickness of 30 μm-10 mm,

- a top layer of for example polyurethane lacquer with a layer thickness of 5 μm-2 mm.

The production of a multilayer coating is carried out according to the invention by

a) introducing the gel-like primer into a mould by knife application, pouring, spraying, injecting;

b) applying the top layer by means of knife coating, pouring, spraying, injecting;

c) arbitrary variation of a) and b) as regards order, e.g.

  - first applying the top layer to the mould wall and then applying the primer;

  - first applying the primer and then applying the top layer to the primer, followed by reaction in a closed or open mould;

  - first applying the primer and then applying the top lacquer to the mould wall, followed by reaction in a closed mould;

d) introduction of the carrier material to be coated into the mould by

e) injection (e.g. plastics materials, thermosetting materials, etc.),

f) insertion (e.g. metal, textile material, wood, finished structural parts),

g) knife application, pouring, spraying (e.g. films, polyurethane lacquer, sprayed skins),

h) application of the primer and of the top lacquer with the variations described in a) and b), to the carrier material to be coated, hardening of the coating, and removal of the finished coated structural part from the mould,

i) production of the primer and of the top lacquer in the mould followed by introduction of the carrier material to be coated into the mould, reaction, and removal of the finished coated structural part.

Different multilayer structures are possible according to the invention, having for example the following construction:

a) top lacquer/primer/top lacquer;

b) top lacquer/primer/top lacquer/carrier (preparation according to a) followed by application to any suitable carrier by the known bonding techniques with for example 1-component or 2-component polyurethane adhesives);

c) top lacquer/primer/carrier/primer/top lacquer;

d) carrier 1/primer/top lacquer/carrier 2 with carrier 1, for example films, textile material and carrier 2 as arbitrary materials described in 10.

The invention also provides for the use of the polyurethane systems according to the invention for coatings that require a special handling behaviour (haptic properties), for example that should exhibit a soft handling behaviour (soft-feel haptic property).

The desired haptic properties are obtained on the one hand through the content of flexible polyols based on polyester, polyester/polyacrylate or polyacrylate (optionally a mixture of OH-functional and non-functional polyols). The conventional fillers and additives that are used may also influence the haptic properties.

All lacquer systems according to the invention can be processed by conventional procedures. In particular the application in the IMC (in-mould coating) process is covered by the invention. This process involves the application of the lacquers in one or both halves of the mould, the gel-like primer is produced between the mould halves as described in EP-A 005 783, and the complete coating can be removed from the mould and then applied to any suitable carrier (metal, wood, plastics, ceramics, stone, concrete, glass, mineral substrates, etc.).

It is also possible to produce a structural part directly in the mould by:

- adding the material to be coated to a mould,
- coating a mould half with
    - mould release agents known in polyurethane chemistry (for example stearate),
    - the top layer of polyurethane lacquer, followed by drying this lacquer on the mould surface,
- closing the two halves of the mould,

- injecting the gel-like primer between the top layer and the carrier,

- removal of the complete structural part consisting of carrier/primer/top layer.

The polyurethane systems according to the invention (primer + top layer) may be used to produce a very wide range of coating systems. The following combinations in particular may be mentioned:

- carrier (wood, metal, glass, ceramics, plastics, rubber, films, polyurethane lacquer),

- gel-like primer (coloured, colourless, transparent, fluorescing, containing active substances, releasing active substances, translucent, containing fragrances),

- polyurethane top lacquer (coloured, colourless, transparent, fluorescing, containing fragrances, translucent, metallic colour effect, soft effect).

The present invention also provides a process for producing the coating system according to the invention comprising

I) substantially anhydrous gel compositions optionally containing active substances, characterised in that

a) one or more diisocyanates and/or polyisocyanates is/are reacted with

b) one or more polyhydroxyl compounds with a molecular weight between 1000 and 12000, and an OH number between 20 and 112,

c) optionally 0.1 to 50 wt.% of active substances,

d) optionally catalysts for the reaction between isocyanate and hydroxyl groups,

e) as well as optionally fillers and additives known *per se* from polyurethane chemistry, wherein the isocyanate index is between 15 and 50, the mathematical product of the functionalities of the polyurethane-forming components is at least 5.2 and the polyhydroxyl compounds are substantially free of hydroxyl compounds with a molecular weight below 800, and

II) in addition a polyurethane coating

is applied to this gel (I) by spraying, knife coating or other application techniques.

In accordance with the invention the top lacquer of the component II) may be applied later, or preferably by application to the wall or walls of the mould in which the gel is produced, followed by gel formation in this mould.

As now claimed according to one aspect, the present invention provides a coating system comprising I) an anhydrous, gel-like, high molecular weight polyurethane composition, which may contain an active substance, comprising (1) 15 to 62 wt.%, based on the weight of (1) and (2), of a high molecular weight covalently crosslinked polyurethane matrix, (2) 38 to 85 wt.%, based on the weight of (1) and (2), of a liquid dispersing agent firmly bound in the matrix by secondary valence bonds, wherein the liquid dispersing agent contains one or more polyhydroxyl compounds having a number average molecular weight of 1000 to 12000 and an OH number of 20 to 112, wherein the dispersing agent is substantially free from hydroxyl compounds having a molecular weight below 800 and (3) optionally 0.1 to 100 wt.%, based on the weight of (1) and (2), of fillers, additives, and/or catalysts for the polyurethane-forming reaction, wherein optionally 0.1 to 50 wt.% of the additives are active substances, and II) a solvent-containing, solvent-free and/or aqueous polyurethane topcoat comprising a) 0 to 50 wt.%, based on the total weight of the topcoat, of a polyurethane adduct, b) 0 to 90 wt.%, based on the total weight of the topcoat, of a flexible polyol having a T_g of -100 to 25°C and an OH content of 0 to 25 wt.%, based on the total weight of the flexible polyol and c) 1.7 to 60 wt.%, based on the total weight of the topcoat, of a polyisocyanate having an NCO content of 4 to 50 wt.%

The polyols to be used according to the invention for the gel-like primer are preferably the polyhydroxypolyesters, polyhydroxypolyethers, polyhydroxypolythioethers, polyhydroxypolyacetales, polyhydroxypolycarbonates or polyhydroxypolyester amides in the molecular weight range, OH number range and having the OH functionality specified above, known *per se* in polyurethane chemistry and liquid at room temperature or slightly above room temperature.

The hydroxyl group-containing polyesters that may be used are for example reaction products of polyhydric, preferably dihydric and optionally in addition trihydric and tetrahydric alcohols with polybasic, preferably dibasic carboxylic acids. Instead of the free polycarboxylic acids, the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or their mixtures may also be used to produce the polyesters. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may optionally be substituted, for example by halogen atoms, and/or unsaturated.

Examples of such polycarboxylic acids and their derivatives that may be mentioned include adipic acid, sebacic acid, phthalic acid, phthalic anhydride, tetrahydrophthalic anhydride or hexahydrophthalic anhydride, isophthalic acid, trimellitic acid, maleic anhydride, dimerised and trimerised unsaturated fatty acids, dimethyl terephthalate and terephthalic acid bis-glycol ester.

Suitable polyhydric alcohols are for example ethylene glycol, propylene glycol, butanediol-1,4 and/or –2,3, hexanediol-1,6, neopentyl glycol, 1,4-bis-hydroxy-methylcyclohexane, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, hexanetriol-1,2,6, pentaerythritol, quinitol, mannitol, and sorbitol, formitol, methyl glycoside, as well as di-, tri-, tetra- and higher polyethylene, polypropylene as well as polybutylene glycols.

The polyesters may contain a proportion of terminal carboxyl groups. Polyesters of lactones, e.g. ε-caprolactone or hydroxycarboxylic acids, for example 8-hydroxy-carboxylic acids, for example hydroxycaproic acid, may also be used.

The polyols containing at least 2, as a rule 2 to 8 and preferably 2 to 3 hydroxyl groups that may also be used according to the invention are those of the type known *per se* and are produced for example by homopolymerisation of epoxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin, for example in the presence of Lewis catalysts, or by addition of these epoxides, preferably ethylene oxide and propylene oxide, optionally as a mixture or in succession, to starting components having reactive hydrogen atoms such as water, alcohols, ammonia or amines, e.g. ethylene glycol, propylene glycol, diethylene glycol, diethylolpropane, glycerol, sorbitol, sucrose, formitol or formose, as well as 1-(4,4′-dihydroxydiphenyl)propane, aniline, ethylenediamine or ethanolamine.

Polythioethers, polybutadienes, polyacetals, polycarbonates or polyester amides containing OH groups may also be used as starting products. Also suitable are polyhydroxyl compounds already containing urethane and/or urea groups, as well as optionally modified natural polyols such as castor oil.

Polyhydroxyl compounds that contain high molecular weight polyadducts and/or polycondensates or polymers in finely dispersed or dissolved form may optionally also be used according to the invention. Such polyhydroxyl compounds are obtained for example by carrying out polyaddition reactions (e.g. reactions between polyisocyanates and aminofunctional compounds) or polycondensation reactions (e.g. between formaldehyde and phenols and/or amines) *in situ* in the hydroxyl group-containing compounds mentioned above.

The polyhydroxyl compounds modified by vinyl polymers, such as are obtained for example by the polymerisation of styrene and/or acrylonitrile in the presence of polyethers or polycarbonate polyols, are also suitable for the process according to the invention.

Examples of the aforementioned high molecular weight polyhydroxyl compounds to be used according to the invention are listed for example in High Polymers, Vol. XVI, “Polyurethanes, Chemistry and Technology”, edited by Saunders – Frisch, Interscience Publishers, New York, London, Vol. I, 1962, pp. 32-42 and pp. 44-54 and Vol. II, 1964, pp. 5-6 and 198-199, and also in Kunststoff-Handbuch, Vol. VII, Vieweg-Höchtlen, Carl-Hanser-Verlag, Munich, 1966, for example on pages 45 to 71, as well as in DE-A 29 20 501, pp. 17 to 24. Obviously mixtures of the aforementioned compounds, for example mixtures of polyethers and polyesters, may be used.

The polyhydroxyl polyethers of the aforementioned type known *per se* in polyurethane chemistry and containing 2 to 6, particularly preferably 2 to 3 hydroxyl groups in the molecule and with a statistically or segmentally incorporated ethylene oxide content of at least 10 wt.%, preferably more than 15 wt.% and particularly preferably of at least 20 wt.%, are preferably used as high molecular weight polyols according to the invention. Most particularly preferred are polypropylene ether polyols with at least 20 wt.% of ethylene oxide, in which at least 15 wt.% of the OH terminal groups are primary hydroxyl groups.

The content of polyols in the gel-forming mixture to be used according to the invention is about 80 – 99 wt.%, preferably about 85 to 98 wt.%, referred to the total weight of the gel-forming mixture of polyurethane starting components.

The following compounds may be mentioned as examples of flexible, solvent-containing, solvent-free or aqueous polyols for the polyurethane top layer that are suitable according to the invention:

1) linear polyester polyols with an OH content of 1-25 wt.% and a viscosity of 100-5000 mPa·s, such as for example Desmophen® 670, Desmophen® VP LS 2328 or Bayhydrol® PT 241;
2) hydroxyfunctional polycarbonate-polyesters with an OH content of 1-10 wt.% and a viscosity of 1500-10000 mPa·s, such as for example Desmophen® VP LS 2236 and Desmophen® C 200;

3) PES/PAC dispersions such as for example Bayhydrol® VP LS 2058;

4) polyether polyols with an OH content of 1-25 wt.% and a viscosity of 100-3000 mPa·s, such as for example Desmophen® 550U;

5) polyurethane adducts with a viscosity of 100-55000 mPa·s, such as for example Impranil® C, Desmolac® 4340 (for example based on IPDI, HDI, W, NTI) or Bayhydrol® DLN.

In principle all elastic polyols having a suitable elongation and rebound behaviour are suitable.

It has been found by experience that flexible polyols have a poorer resistance to solvents, chemicals, outdoor weathering and short-term weathering than comparably brittle polyols based on polyesters or polyacrylates.

Mixtures of flexible and brittle polyols may be used for the production of the polyol component according to the invention.

The following may be mentioned as examples of solvent-containing, solvent-free or aqueous polyols for improving the resistance properties that are suitable according to the invention:

1) hydroxyfunctional polyester polyacrylates with an OH content of 1-22 wt.% and a viscosity of 1000-5000 mPa·s, such as Desmophen® Laborprodukt TIK 294, Bayhydrol® VP LS 2290;
2) low viscosity polyacrylate polyols/polymethacrylate polyols with an OH content of 1-23 wt.% and a viscosity of 700-1500 mPa·s, such as Desmophen ® Laborprodukt TIK 507 and Desmophen® Laborprodukt TIK 516 and Bayhydrol® VP LS 2235/1;

3) branched polyester polyols with an OH content of 12-20 wt.% and a viscosity of 1000-4000 mPa·s, such as Desmophen® VP LS 2249/1.

Unless otherwise stated the same conditions apply for polyols as in the descriptions of the polyols for the polyurethane primer above.

The organic diisocyanates and/or polyisocyanates to be used in the gel-like primers according to the invention are the aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic diisocyanates and/or polyisocyanates known *per se* in polyurethane chemistry, such as are described for example by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pp. 75 to 136, wherein the diisocyanates may be used as monomers or in modified form, for example biuretised, allophanated, carbodiimidised, trimerised or polyol-modified. The following may be mentioned by way of example: 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, and also cyclobutane-1,3-diisocyanate, cyclohexane-1,3 and cyclohexane-1,4-diisocyanate, as well as arbitrary mixtures of these position isomers and/or stereoisomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diisocyanate, hexahydro-1,3- and/or hexahydro–1,4-phenylene diisocyanate, perhydro-2,4′- and/or –4,4′-diphenylmethane diisocyanate, as well as arbitrary mixtures of these position isomers and/or stereoisomers, and in addition 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6- toluylene diisocyanate, diphenylmethane-2,4′- and/or diphenylmethane-4,4′-diisocyanate, as well as arbitrary mixtures of their isomers, and naphthylene-1,5- diisocyanate.

Further examples of suitable isocyanates are the following: triphenylmethane-4,4′,4″ -triisocyanate, polyphenyl-polymethylene polyisocyanates such as are obtained by aniline-formaldehyde condensation followed by phosgenation, and p-isocyanatophenylsulfonyl isocyanates, perchlorinated arylpolyisocyanates, carbodiimide group-containing polyisocyanates, norbornane diisocyanates, allophanate group-containing polyisocyanates, isocyanurate group-containing polyisocyanates, urethane group-containing polyisocyanates, polyisocyanates containing acylated urea groups, biuret group-containing polyisocyanates, polyisocyanates produced by telomerisation reactions, ester group-containing polyisocyanates, reaction products of the aforementioned isocyanates with acetals, and polyisocyanates containing polymeric fatty acid esters. These polyisocyanates suitable for the reaction are described in detail in EP-A 0 057 839. Preferred aromatic diisocyanates and triisocyanates are 2,4- and/or 2,6-toluylene diisocyanate, and 4,4'-and/or 2,4'-diphenylmethane diisocyanate and their modified types, as well as their multifunctional derivatives or trimerisation products produced with trihydric and tetrahydric polyols.

Preferred polyisocyanates are for example 1,6-hexamethylene diisocyanate, isophorone diisocyanate, methylcyclohexane-2,4- and/or methylcyclohexane–2,6-diisocyanate, dicyclohexylmethane-2,4'- and/or dicyclohexylmethane-4,4'-diisocyanates and their biuretised, allophanated or trimerised polyfunctional derivatives.

All the aforementioned diisocyanates and/or polyisocyanates may be used as arbitrary mixtures. The content of diisocyanates and/or polyisocyanates in the gel-forming mixtures of polyols and polyisocyanates is ca. 1 to 20 wt.%, preferably 2 to 15 wt.%, referred to the total weight of the mixture.

The catalysts to be used for the reaction between hydroxyl groups and isocyanate groups in the gel formation are preferably those that are known *per se* in polyurethane chemistry, for example tertiary amines such as triethylamine, N-tetramethylenediamine, 1,4-diaza-bicyclo-(2,2,2)-octane, N,N-dimethylbenzylamine, X-methyl-KI-dimethylaminoethyl piperazine, pentamethyldiethylenetriamine; also suitable as catalysts are known Mannich bases formed from secondary amines such as dimethylamine, and aldehydes (formaldehyde) or ketones (acetone) and phenols, as well as silamines with carbon-silicon bonds, for example 2,2,4-trimethyl-2-silamorpholine and 1,3-diethylaminomethyltetramethyldisiloxane.

According to the invention organometallic compounds, in particular organotin compounds may also be used as catalysts, for example tin-(II)-acetate, tin-(II)ethylhexoate and tin-(IV) compounds, for example dibutyltin dichloride, dibutyltin dilaurate and dibutyltin maleate. Further suitable catalysts are described in DE-A 29 20 501 on p.29, line 5, to p.31, line 25.

The catalysts are preferably used in an amount of between 0.01 and 10 wt.%, referred to the total weight of the gel. All catalysts may obviously also be used in the form of mixtures.

The additives described in EP-A 0 057 389 (active substances, fillers, additives, auxiliary substances) may also be used according to the invention.

In the hardener component according to the invention for the top layer, there are preferably used aliphatic polyisocyanates based on low viscosity polymers of 1,6-hexamethylene diisocyanate (HDI), 4,4′-diisocyanatodicyclohexyl isocyanato-urethane (W), triisocyanatononane (NTI, TIN) or isophorone diisocyanate (IPDI), which may be employed individually or in combination. If the aliphatic polyisocyanates do not have to exhibit light-fastness, then the known aromatic polyisocyanates may also be used (for example MDI or TDI).

The following may be mentioned as examples of polyisocyanates for sole use according to the invention or for use in combinations according to the invention (solvent-containing, solvent-free or aqueous systems) in component II:

1) low viscosity polyisocyanates based on biurets of HDI with a content of 15-24 wt.% and a viscosity of 100-4000 mPa·s, such as Desmodur® N 75 and Desmodur® N 3200;

2) low viscosity trimers of HDI and their modifications with allophanate and uretdione with an NCO content of 12-25 wt.% and a viscosity of 100-4000 mPa·s, such as Desmodur® VP LS 2102, Desmodur® N 3300, Desmodur® N 3400, Desmodur® N 3600 or Bayhydur® 3100;

3) elasticising polyisocyanates with an NCO content of 4-25 wt.% and a viscosity of 1000-10000 mPa·s, such as for example Desmodur® VP LS 2010/1 or Bayhydur® VP LS 2306;

4) triisocyanatononane with an NCO content of 48-52 wt.% at a viscosity of 10-100 mPa·s;

5) mixtures of trimers of IPDI and trimers and/or the uretdione of HDI with an NCO content of 15-22 wt.% and a viscosity of 1000-5000 mPa·s;

6) polyisocyanates based on H_{12}-MDI with an NCO content of 10-33 wt.% and a viscosity of 20-10000 mPa·s, such as for example Desmodur® W;

7) blocked polyisocyanates such as Desmodur® VP LS 2253 or Desmodur® VP LS 2307;

8) as well as, similarly, the remaining polyisocyanates as described above for the polyurethane primer.

The lacquers produced from the polyurethane systems according to the invention are coloured using the pigments and fillers conventionally used for lacquer production. Particularly suitable are for example inorganic pigments based on for example iron oxide (e.g. Bayferrox® 318M) or titanium dioxide (e.g. Tronox® RKB-4). All known colour effect pigments may also be used.

As catalyst for the production of the top lacquers from the polyurethane systems according to the invention, there are used the known substances employed for two-component polyurethane systems, such as for example organic compounds of tin (e.g. dibutyltin dilaurate or dibutyltin diacetate) or organic compounds of zinc (e.g. zinc octoate). The amount varies depending on the system that is used, the required reaction time and the nature of the catalyst, and is between 0.01 and 3.0 wt.% of the catalyst, referred to the resin fraction of the system.

The following methods may be used for example to process the systems according to the invention:

The described systems may be applied by knife coating, pouring or spraying to any suitable substrate or in any suitable mould, and depending on the lacquer composition are dried at room temperature or under forced conditions, for example for 10-30 minutes at 60-120°C.

After the films have hardened highly elastic coatings are obtained (elongation up to more than 600%) with good rebound properties. The other film properties satisfy at least the usual standards in conventional polyurethane chemistry.

The production of the gel primer according to the invention and containing active substances may be carried out continuously or batchwise. The procedure depends, *inter alia*, on the shape that is to be imparted to the gels according to the invention having regard to their use. The one-shot or the prepolymer process may be employed.

In the one-shot process all components, i.e. polyols, diisocyanates and/or polyisocyanates, active substances, catalysts and optionally further fillers and additives are added in one go and intensively mixed with one another, the active substances preferably being dissolved or dispersed in the polyol components.

In the prepolymer process two procedures are possible. Either an isocyanate prepolymer is produced first of all by reacting a corresponding proportion of the polyol amount (+ active substance) of the total amount of isocyanate intended for the gel formation, and then adding the remaining amount of polyol (optionally with further active substances), as well as optionally further fillers and additives, to the prepolymer obtained and intensively mixing the whole, or the total amount of polyol (+ active substance) intended for the gel formation is reacted with part of the polyisocyanate amount to form an OH prepolymer, following which the remaining amount of polyisocyanate is mixed in.

A particularly advantageous procedure according to the invention is a variant of the one-shot process and the OH-prepolymer process. In this case the polyol or polyol mixture, the active substances, optionally the fillers and additives, the catalyst and two different diisocyanates are combined in one shot and intensively mixed, one diisocyanate or polyisocyanate being aromatic in nature and one diisocyanate and/or polyisocyanate being aliphatic in nature. It may be assumed that, due to the markedly different reactivity of the two polyisocyanates, a hydroxyl prepolymer is first formed, which then reacts within a few minutes with the other polyisocyanate with gel formation. Gels with a particularly high toughness are thereby obtained.
In these procedures the conveying, metering in and mixing of the individual components or component mixtures may be performed using equipment known *per se* to the person skilled in the art in polyurethane chemistry.

If for example mouldings are to be produced for direct use, then the batch procedure is preferred. If however the polyurethane gel according to the invention is to be produced in unit pieces of suitable dimensions, then a continuous procedure is often more favourable. In this case an endless film or sheet is first of all produced, which can then be cut up into individual pieces and lacquered.

With continuous production the gellable mixture optionally containing active substances can also be sprayed, poured or knife coated before it has solidified due to the gel formation. The gellable mixture containing active substances can be applied to a very wide variety of materials based on natural or synthetic raw materials, for example to mats, fleece, knitted fabrics, hosiery, expanded films, plastics films or sheets, or may be cast in desired shapes.

The invention also provides for the use of the coatings systems according to the invention in the IMC (in-mould coating) process.

In the IMC process the component II)

a) is applied (by spraying, knife coating, brush application, etc.) to one or both halves of the mould (depending on the arrangement and articles to be formed) and is gently dried (preferably at room temperature or slightly elevated temperatures). The component I) is then added to the mould by the methods described above, hardened together with the component II), following which the coated moulding is removed from the mould,

b) is subsequently injected (after the production of the component I)) into a defined gap in the mould (possible only in the solvent-free variant) and is then hardened together with component I), and

c) the composite produced from a) and b) is then applied to the object to be coated.

In a particular embodiment the objects to be coated may also be introduced into a mould and then coated according to the invention in the latter.

The conditions during the gel formation can also be varied so that either compact or foamed gels are obtained. If for example air is injected into the gellable mixture, then foamed gels are obtained.

Objects can also be moulded according to the invention, for example by decanting the body to be moulded together with a gel-forming composition and removing the moulding after the gel formation.

According to the invention multilayer coatings can be produced from

- a gel-like primer with a layer thickness of 30 µm–10 mm, and

- a top layer of polyurethane lacquer with a layer thickness of 5 µm–2 mm.

Multilayer coatings can be produced using the coating systems according to the invention by the following steps, the order of which is not fixed:

a) addition of the gel-like primer to a mould by knife coating, pouring, spraying, injecting,

b) application of the top layer by knife coating, pouring, spraying, injecting,

c) wherein a) and b) may be varied as follows as regards order

  - firstly application of the top layer to the mould wall and then addition of the primer,

  - firstly addition of the primer and then application of the top lacquer to the primer and reaction in a closed or open mould,

- firstly addition of the primer and then application of the top lacquer to the mould wall and reaction in a closed mould,

d) introduction of the carrier material to be coated into the mould by

e) injection (e.g. plastics materials, thermoplastics, etc.)

f) application (e.g. to metals, textiles, wood, finished structural parts),

g) knife coating, pouring, spraying (e.g. films, polyurethane lacquer, sprayed skins),

h) application of the primer and top lacquer with the variations described in a) and b) to the carrier material to be coated, hardening of the coating, and removal of the finished coated structural part from the mould,

i) production of the primer and top lacquer in the mould followed by introduction of the carrier material to be coated into the mould, reaction, and removal of the finished coated structural component.

Multilayer structures of different composite construction may be produced within the scope of the invention, for example

a) top lacquer/primer/top lacquer,

b) top lacquer/primer/top lacquer/carrier, followed by application to the carrier using bonding techniques with for example one-component or two-component polyurethane adhesives,

c) top lacquer/primer/carrier/primer/top lacquer,

d) carrier 1/primer/top lacquer/carrier 2 together with carrier 1 such as films, textile materials and carrier 2 as in arbitrary materials described in 10.

The coating systems according to the invention are suitable for coating a very wide variety of substrates of widely varying geometrical shapes, such as smooth flat surfaces, films, sheet materials, hollow bodies (external and internal), etc. The substrates to be coated may consist of different materials as well as of composite materials, and may for example consist of stone, mineral substances, glass, plastics, wood, metals, semi-metals (e.g. Si), fibrous substances, pressed substrates or polyurethane foams.

The coatings according to the invention are furthermore suitable for the accurate forming of models from a very wide variety of materials, such as for example gypsum, wood, concrete, steel, plastics such as epoxides or polyurethanes, stone, ceramics or metals such as copper and iron, as well as for producing artificial bones, joints, dental plates and dentures. These articles are then provided with a multilayer coating.

Examples of polyurethane top lacquer

Formulation 1

A)	Desmophen® 670, 80% in butyl acetate (MPA)	33.6 wt.%
	1-methoxypropylacetate-2	48.8 wt.%
	dibutyltin dilaurate, 10% in MPA	0.1 wt.%
B)	Desmodur® N 75, 75% in MPA/xylene	17.5 wt.%
		100.0 wt.%

Formulation 2

A)	Impranil® C, 30% in ethyl acetate	31.9 wt.%
	Desmophen® 670, 80% in MPA	11.9 wt.%
	MPA	48.0 wt.%
B)	Desmodur® N 75, 75% in MPA/xylene	8.2 wt.%
		100.0 wt.%

Formulation 3

A)	Impranil® C, 30% in ethyl acetate	67.7 wt.%
	Desmophen® 670, 80% in MPA	6.3 wt.%
	MPA	18.8 wt.%
B)	Desmodur® N 75, 75% in MPA/xylene	5.5 wt.%
	Desmodur® VP LS 2010/1, 100%	1.7 wt.%
		100.0 wt.%

Formulation 4

A)	Impranil® C, 30% in ethyl acetate	45.7 wt.%
	Desmolac® 4340, 40% in xylene/isobutanol	11.4 wt.%
	MPA	40.1 wt.%
B)	Desmodur® N 75, 75% in MPA/xylene	2.8 wt.%
		100.0 wt.%

Formulation 5

A)	Impranil® C, 30% in ethyl acetate	48.4 wt.%
	Desmolac® VP LS 2195/1, 40% in butylacetate/NMP	12.1 wt.%
	MPA	36.5 wt.%
B)	Desmodur® N 75, 75% in MPA/xylene	3.0 wt.%
		100.0 wt.%

Formulation 6

A)	Impranil® C, 30% in ethyl acetate	37.6 wt.%
	Desmophen® 1652, 100%	11.2 wt.%
	MPA	45.3 wt.%
B)	Desmodur® VP LS 2010/1, 100%	5.9 wt.%
		100.0 wt.%

Formulation 7

A)	Impranil® C, 30% in ethyl acetate	74.0 wt.%
	MPA	22.3 wt.%
B)	Desmodur® N 75, 75% in MPA/xylene	3.7 wt.%
		100.0 wt.%

Formulation 8

A)	Bayhydrol® VP LS 2244/1	48.7 wt.%
	Bayhydrol® PR 240	48.7 wt.%
B)	Desmodur® VP LS 2307	2.6 wt.%
		100.0 wt.%

Examples of polyurethane primer

Examples 1 to 10 of EP-A 57838 were used for the primer.

The wording of Examples 1 to 10 of EP-A 57838 is as follows:

Example 1 (from EP-A 57 838)

3500 parts of a polyether based on trimethylolpropane with a hydroxyl number of 56, produced from 45% propylene oxide and 55% ethylene oxide, 700 parts of a polyether based on trimethylolpropane with a hydroxyl number of 34, produced from 83% propylene oxide and 17% ethylene oxide, and 2800 parts of a polyether based on propylene glycol with a hydroxyl number of 56, produced from 100% propylene oxide, are stirred at a temperature of 22°C by means of a laboratory mixer equipped with a stirring disc to form a clear solution. 301 parts of a biuret polyisocyanate with an isocyanate content of 21 wt.%, a mean functionality of 3.6 and a mean molecular weight of 700, which was produced by biuretisation reaction from hexamethylene diisocyanates (Desmodur N® from Bayer AG) are added to this solution while stirring and thoroughly distributed. 105 parts of dibutyltin dilaurate are added to the now turbid solution and the mixture is intensively mixed for 3 minutes. The whitish turbid solution is poured into a prepared square casing of polyurethane film of film thickness 0.2 mm with an edge length of 45 cm and the film casing is sealed in an airtight manner. The thus prepared gel cushion is placed on a flat support and left by itself for the gel reaction to take place, following which the gel cushion reaches its mechanical final strength and can be fully loaded. The cushion is a soft, dimensionally stable body deformable under pressure. When the deforming force is lifted, the gel cushion returns to its original state.

Under loading with an artificial seat made from plastics material and loaded with a 35 kg weight, a pressure of 44 pressure units (PU) is measured on the crosspiece and a pressure of 48 PU is measured on the seat leg projections.

Example 2 (Comparison Example from EP-A 57 838)

A foam cushion made from a commercially available polyether foam with a bulk density according to DIN 53 420 of 35 kg/m^3 and a compressive strength (40%)

according to DIN 53 571 of 3.3 KPa, as is conventionally used for the production of cushion units and mattresses, is provided with a film covering of polyurethane film, such as is used in Example 1. The cushion covered in this way is loaded similarly to Example 1 with an artificial seat. A pressure of 109 PU is measured on the crosspiece and a pressure of 34 PU is measured on the seat leg projection.

Example 3 (from EP-A 57 838)

A gel-forming mixture is produced according to the procedure described in Example 1 and is poured, similarly to Example 1, into a square covering made of elastic film. However, instead of being fabricated from a 0.2 mm thick polyurethane film, the covering is fabricated from a polymer blend consisting of 50 parts of polypropylene and 50 parts of a styrene-butadiene block copolymer.

After the gel reaction is complete, a soft, dimensionally stable gel cushion deformable under pressure is obtained, which after deformation returns to its original state when the deforming force is lifted.

The gel cushion obtained in this way is loaded similarly to Example 1 with an artificial seat. A pressure of 18 PU is measured on the crosspiece and a pressure of 19 PU is measured on the seat leg projections.

Example 4 (from EP-A 57 838)

A gel-forming mixture is produced according to the procedure described in Example 1 and poured similarly to Example 1 into a square covering. However, instead of being fabricated from polyurethane film the covering is fabricated from an elastic textile provided with an elastic polyurethane coating, such as is generally customary and known for example in the manufacture of corsetry or bathwear.

After the gel reaction is complete a soft, dimensionally stable gel cushion deformable under pressure is obtained, which after deformation returns to its original state when the deforming force is lifted. The gel cushion obtained in this way is loaded similarly to Example 1 with an artificial seat. A pressure of 32 PU is measured on the crosspiece projection and a pressure of 28 PU on the seat leg projections.

Example 5 (from EP-A 57 838)

3500 parts of a polyether based on trimethylolpropane with a hydroxyl number of 56, produced from 45% propylene oxide and 55% ethylene oxide, 700 parts of a polyether based on trimethylolpropane with a hydroxyl number of 34, produced from 83% propylene oxide and 17% ethylene oxide, and 2800 parts of a polyether based on propylene glycol with a hydroxyl number of 56, produced from 100% propylene oxide, and 35 parts of dibutyltin dilaurate are homogeneously mixed in a stirrer vessel at 22°C. The mixture is added by means of a gear-type pump to a static mixer. 273 parts of the biuret polyisocyanate from Example 1 are added at the same time from a separate storage container to this mixer using a further gear-type pump so that the mixing ratio of the two components is equal at all times and corresponds to the ratio of the total amounts.

The whitish turbid solution flowing out from the static mixer is poured into a square covering, as was described in Example 4, and a gel cushion in the form of a pillow is made therefrom as described in Example 1.

After the gel reaction is complete, a soft, dimensionally stable gel cushion deformable under pressure is obtained, which after deformation returns to its original state when the deforming force is lifted.

The gel cushion obtained in this way is loaded with an artificial seat as described in Example 1. The following pressure values are measured: crossleg projection 31 PU; seat leg projections 23 PU.

Example 6 (from EP-A 57 838)

1000 parts of a polyether based on trimethylolpropane with a hydroxyl number of 35, produced from 80% propylene oxide and 20% ethylene oxide, 50 parts of the biuret polyisocyanate from Example 1, and 15 parts of dibutyltin dilaurate are intensively mixed within 1 minute at room temperature using a laboratory stirrer with a stirring disc. After 10 minutes an opaque, elastic, colour-stable gel is obtained which can easily be deformed under the influence of a force acting thereupon and which adopts its original state after the deforming force is lifted.

The gel is particularly suitable for producing gel cushions.

Example 7 (from EP-A 57 838)

1000 parts of a polyether based on sorbitol with a hydroxyl number of 46, produced from 100% propylene oxide, 25 parts of toluylene diisocyanate (80% 2,4-isomer and 20% 2,6-isomer) and 30 parts of dibutyltin dilaurate are intensively mixed within 1 minute at room temperature using a laboratory stirrer with a stirring disc. A soft, elastic, dimensionally stable gel is obtained which can easily be deformed under the influence of a force acting thereupon and which returns to its original state after the deforming force is lifted.

The gel is likewise particularly suitable for producing gel cushions.

Example 8 (from EP-A 57 838)

1000 parts of a polyether according to Example 7, 45 parts of 4,4′-diisocyanatodiphenylmethane that has been modified by urethanisation reaction with tripropylene glycol and has an isocyanate content of 23%, and 30 parts of dibutyltin dilaurate are reacted using a laboratory stirrer according to Example 7. A soft, elastic, dimensionally stable gel is obtained which can easily be deformed under the influence of a force acting thereupon and which returns to its original state after the deforming force is lifted.

The gel is likewise suitable for producing gel cushions.

Example 9 (from EP-A 57 838)

1000 parts of a polyether based on glycerol with a hydroxyl number of 28, produced from 40% propylene oxide and 60% ethylene oxide, are reacted with 50 parts of the polyisocyanate according to Example 8 and 30 parts of dibutyltin dilaurate analogously to Example 7 to form a soft, elastic, dimensionally stable gel that can easily be deformed under the influence of a force acting thereupon and which returns to its original state after the deforming force is lifted. The gel is likewise suitable for producing gel cushions.

Example 10 (from EP-A 57 838)

The example illustrates the co-use of plasticisers. 490 parts of a polyether based on trimethylolpropane with a hydroxyl number of 56, produced from 45% propylene oxide and 55% ethylene oxide, 480 parts of dibutyltin adipate, 30 parts of the isocyanate according to Example 1 and 15 parts of dibutyltin dilaurate are reacted according to Example 7 to form a soft, elastic, dimensionally stable gel that can easily be deformed under the influence of a force acting thereupon and which returns to its original state after the deforming force is lifted. The gel may likewise be used to produce gel cushions.

Examples of Application:

1. Multilayer IMC Process

The cover layer material (component II) according to the invention is produced by constant stirring in, for example using a dissolver or blade mixer (e.g. compressed air stirrer 756D3 from Otto Bock Helthcare). Care should be taken to ensure that all additives involved in the quality of the surface, such as for example matting agents, rheology improvers, agents for improving scratch resistance, lubricants, colouring pigments, etc., are homogeneously incorporated, like known materials used in lacquer technology, with the avoidance of the formation of agglomerates. So that a transparent and translucent cover layer can be produced, it must be ensured before processing the component II that no air bubbles remain in the said component II. So that the component II according to the invention can subsequently easily be removed from the moulds, the mould surfaces are sprayed with separating agents known in PUR technology.

In the charging operation the component II is introduced into the preheated moulds using commercially available lacquering guns (e.g. Coating Set 746B20 from Otto Bock Helthcare, Duderstadt). Care should be taken to avoid material agglomerations since these influence the appearance and touch and handling of the surface. The injection pressure and material pressure of the injection tool should be adjusted so that the desired cover layer thickness and desired surface properties are achieved.

The component II must be flashed-off until solvent can no longer be detected (finger and smell test). The flashing-off and drying of the component II may be accelerated by heating.

In the IMC process the following variants are also possible:

a) Both halves of the mould are lacquered with several layers of the component II, optionally with the aid of masking stencils. The mould is closed and sealed manually, semi-automatically or fully automatically with commercially available closure units after the component II has dried. The component I is introduced into the closed mould by means of low pressure machines conventionally used in PUR technology. In order that no air bubbles are formed in the moulded part, the riser and the sprue must match the respective geometry. After the component II has reacted the mould is opened and the moulded part is removed. So that the final strength of the components I and II is achieved, the moulded part must be tempered for a further 72 hours at ambient temperature or for a correspondingly shorter time in an hot air oven at ca. 40° to 80°C.

b) The two-part or multipart mould halves are lacquered according to the description under point 1a). A load-supporting insert consisting for example of wood, plastics, metal, other materials as well as combinations thereof, is secured on one half of the mould. The mould is closed and the insert is encased in the component I. The interlaminar bonding between the component I and the insert should be checked, and if necessary should be improved using commercially available primers or coupling agents. So that the final strength of the components I and II is achieved, the moulded part must be tempered for a further 72 hours at ambient temperature or for a correspondingly shorter time in an hot air oven at ca. 40° to 80°C. The following structure is formed:

cover layer according to the invention (component II)
gel layer according to the invention (component I)
moulded part carrier
gel layer according to the invention (component I)
cover layer according to the invention (component II)

c) As a further variant, it is possible to clamp a moulded part carrier formed from the materials already mentioned in 1. b) onto one half of the mould. The two halves of the mould are then closed and the component I is injected in. The following structure is formed:

cover layer according to the invention (component II)
gel layer according to the invention (component I)
moulded part carrier

So that the final strength of the components I and II is achieved, the moulded part must be tempered for a further 72 hours at ambient temperature or for a correspondingly shorter time in an hot air oven at ca. 40° to 80°C.

2. Slash Process

In the slash process the solvent-free component II according to the invention is introduced into one half of a mould and the mould is then closed as described in point 1. a). The mould is swivelled corresponding to the geometry so that as uniform a cover layer thickness as possible is formed. After the component II according to the invention has reacted, which can be accelerated by heating, the component I is injected into the mould by means of commercially available two-component machines. Here too corresponding risers should be taken into account. So that the final strength of the components I and II is reached, the moulded part must be tempered for a further 72 hours at ambient temperature or for a correspondingly shorter time in an hot air oven at ca. 40° to 80°C.

3. Dipping Process

In the dipping process contoured parts formed from the component I with and/or without inserts or moulded part carriers are produced in the first step. After the component I has reacted, the moulded part is removed. After it has been cleaned, the moulded part is dipped in a dipping tank filled with the component II. The component II must be adjusted by using more or less solvent so that the desired layer thickness of the component II is obtained. The outer lacquer appearance is influenced by the addition of special additives, such as are conventionally used in general lacquer technology. In the dipping process care should be taken to ensure that the component II is absolutely free of air inclusions since these lead to considerable surface defects. So that the final strength of the components I and II is reached, the moulded part must be tempered for a further 72 hours at ambient temperature or for a correspondingly shorter time in an hot air oven at ca. 40° to 80°C.

4. Knife Blade Process

The component II according to the invention is knife coated by means of a fixed or moving knife blade in one or more layers onto a substrate, such as for example smooth and/or structured paper, films, sheeting, metal and plastics panels, etc. The surfaces to be knife coated must be prepared in such a way that the component II can easily be removed after the production process. This is achieved for example by release agents based on silicone or a Teflon coating on the respective surfaces. In this connection all surface finishes known in PUR technology can also be obtained. After the component II has been sufficiently flashed off, the component I according to the invention is applied. This process permits a continuous production procedure. After the component I has been applied the remaining surface can be laminated with all possible rigid and flexible cover layers. Cover layers are understood in this connection to include for example textiles, with and without a film coating, three-dimensional knitted fabrics, leather, all types of films (see also the book "Nentwig Kunststoff Folien, Hanser-Verlag: ISBN 3-446-17598-9: PE, PP, PET, PVC, PUR, PA, etc., and combinations thereof), sheeting, metal panels, plastics panels, etc. As a result of the structure in the surface to be coated with the component II, a corresponding copy of the said surface structure is obtained on the end product,

5. Lacquering Process

In this process the moulded parts of component I to be coated with the component II according to the invention are produced according to point 3 in a first step. Since the component I is self-adhesive, all shaping surfaces must be coated with separating agents or Teflon coatings, such as are known in PUR technology. The moulded parts to be coated with the component II are removed from the shaping moulds and then lacquered with the component II using commercially available spray guns. The component II may be applied in several layers in order to achieve the desired layer thickness. The outer cover layer should be provided with the additives mentioned for example under point 1 in order to achieve the desired surface quality. So that the final strength of the components I and II is reached, the moulded part must be tempered for a further 72 hours at ambient temperature or for a correspondingly shorter time in an hot air oven at ca. 40° to 80°C.

6.1 IMC/Gel/PUR Foam

In this process the component II according to point 1 and the corresponding subpoints are injected into the mould halves. After the component II has been sufficiently flashed off, the component I is introduced into the recesses provided for this purpose. After the component I has fully reacted, the mould halves are closed and sealed. A flexible foam, semi-rigid foam, integral foam, rigid foam or reaction injection-moulding (RIM) foam for example is introduced into the closed mould. Here too inserts and moulded part carriers may if desired also be used as described under point 1a) and 1b). After the components have hardened the moulded part is removed and tempered as described above.

6.2 IMC/PUR Foam

In this variant the process is as described in point 6.1, except that the component I is omitted.

7.0 IMC/PUR Lacquered Foam

In this method commercially available chopped foams and moulded foams, such as for example composite, cold, integral, compressed, PVC, viscoelastic foams, etc., are subsequently lacquered with the component II according to the invention using a spray gun. The surface can be altered by varying the parameters (material pressure and spraying pressure) of the spray gun, so that for example a closed or open hard-wearing skin is formed on the respective foam.

Multilayer coating system consisting of a thick-layered, gel-like base layer and a cover layer of polyurethane lacquer, its production and use

Process

1a, 1b, 1c) IMC in moulds followed by gel injection

2) Slash process

3) Dipping process

4) IMC on film and structured and unstructured siliconised paper, followed by gel application

5) Lacquer subsequently applied to gel plates and contoured sections

Examples of use:

- Arm rests for office chairs, with integrated nylon supports	1b, 3 5
- Arm rests for office chairs based on moulded carriers	1c, 3, 5
- Seat parts for office chairs	1a
- Bicycle handlebar grips	1b, 3, 5
- Mouse mats	1a, 5
- Neck cushions for washstands	1a, 2, 3, 5

- Neck cushions for baths	1a, 2, 3, 5
- Lordosis cushions	1a, 2, 3, 5
- Panel materials	4
- Inliners for prosthesis shanks	1a, 2, 5
- Contoured parts, plain heels, foot support lining in shoes	1a
- Bicycle saddles	1c
- Steering wheels	1b, 6.1, 6.2

Lacquer composition

- **Lacquer raw material**
- **Mixture of several solvents**
- **Isocyanate**
- **Activator**
- **Additives for shaping the surface**
  - rheology
  - scratch resistance
  - slip property and prevention of run-off
  - colouring additives
  - solvent resistance

- **Spray tool**
  - spray gun with separate device for adjusting the material pressure
  - material pressure 0.3 - 1.5 bar
  - spray pressure 1.5 - 8 bar

- **Compressed air**
  - dry and oil-free
  - adjustable to 1 - 8 bar

- **Moulds**
  - aluminium, structured and unstructured
  - Teflonised, etched, eroded

- **Casting resin**

- **PE films**

- **Structured paper, siliconised**

Operating procedure

- Heating of the mould to ca. 40 - 70°C
- Cleaning of the mould with compressed air
- Charging of the mould release agent with compressed air atomiser
- Application of the lacquer (2 - 8 workstages, crosswise with compressed air gun)
- Drying with air jet or hot air fan
- Insertion and securement of the insert or carrier
- Closure of the mould

- Injection of the gel
- Removal of the complete moulded part
- Tempering of the moulded part for 72 hours at ambient temperature or for several hours at 30-80°C in an hot air oven.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The claims defining the invention are as follows:

1. A coating system comprising

    I) an anhydrous, gel-like, high molecular weight polyurethane composition, which may contain an active substance, comprising

        (1) 15 to 62 wt.%, based on the weight of (1) and (2), of a high molecular weight covalently crosslinked polyurethane matrix,

        (2) 38 to 85 wt.%, based on the weight of (1) and (2), of a liquid dispersing agent firmly bound in the matrix by secondary valence bonds, wherein the liquid dispersing agent contains one or more polyhydroxyl compounds having a number average molecular weight of 1000 to 12000 and an OH number of 20 to 112, wherein the dispersing agent is substantially free from hydroxyl compounds having a molecular weight below 800 and

        (3) optionally 0.1 to 100 wt.%, based on the weight of (1) and (2), of fillers, additives and/or catalysts for the polyurethane-forming reaction, wherein optionally 0.1 to 50 wt.% of the additives are active substances, and

    II) a solvent-containing, solvent-free and/or aqueous polyurethane topcoat comprising

        a) 0 to 50 wt.%, based on the total weight of the topcoat, of a polyurethane adduct,

        b) 0 to 90 wt.% based on the total weight of the topcoat, of a flexible polyol having a T_g of -100 to 25°C and an OH content of 0 to 25 wt.%, based on the total weight of the flexible polyol and

        c) 1.7 to 60 wt.%, based on the total weight of the topcoat, of a polyisocyanate having an NCO content of 4 to 50 wt.%

2. The coating system according to claim 1 wherein polyurethane composition I) contains 20 to 57 wt.% of polyurethane matrix (1) and 43 to 80 wt.% of liquid dispersing agent (2) and polyurethane matrix comprises the reaction product of one or more polyisocyanates and one or more polyhydroxyl compounds with a number average molecular weight of 1000 to 12000 and an OH number between 20 and 112, wherein the mathematical product of the NCO functionality of the polyisocyanates and OH functionality of the polyhydroxyl compounds is at least 5.2.

3. The coating system according to claim 1 or claim 2 wherein liquid dispersing agent (2) comprises one or more polyhdroxyl compounds with a number average molecular weight of 1700 to 6000 and an OH number of 28 to 84.

4. The coating system according to any one of claims 1 to 3 wherein component (3) contains an active substances comprising a member selected from the group consisting of biocides, fragrances, colorants, detergents and washing aids, marking inks and printing inks, anti-ageing agents, lubricants and antistatics, cleaning and care agents, anti-fouling agents, wood protection agents, plant nutrients, preservatives and growth regulators.

5. The coating system according to claim 1 wherein the polyurethane topcoat II) comprises the reaction product of flexible polyol b) with a Tg of -100 to 25°C and an OH content of 0 to 25 wt.% with a polyisocyanate c) and optionally contains up to 50 wt.%, based on the total weight of the topcoat, of a non-crosslinking polyurethane adduct a).

6. The coating system according to claim 1 wherein polyisocyanate c) is present in an amount of up to 40%, based on the total weight of the topcoat.

7. The coating system according to claim 1 wherein flexible polyol IIb) is mixed with a polyacrylate.

8. A multilayer coating produced from the coating system according to claim 1 wherein the polyurethane matrix has a layer thickness of 30µm to 10mm and the polyurethane topcoat has a layer of thickness of 5µm to 2mm.

9. A process for producing the multilayer coating according to claim 8 which comprises
   a) adding the polyurethane matrix to a mould by knife coating, pouring, spraying or injecting,
   b) applying the topcoat by knife coating, pouring, spraying or injecting,
   c) wherein a) and b) may be varied as follows as regards order
      i) applying the topcoat to the mould wall and then adding the primer and reacting in a closed open mould,
      ii) adding the primer and then applying the topcoat to the primer and reacting in a closed or open mould,
      iii) adding the primer and then applying the topcoat to the mould wall and reacting in a closed mould.

10. The process according to claim 9 which comprises introducing a carrier material to be coated into the mould by injection, knife coating, pouring or spraying prior to steps a) and b).

11. The process according to claim 9 which comprises introducing a carrier material into the mould by injection, knife coating, pouring or spraying after to steps a) and b).

12. A coating system substantially as hereinbefore described with reference to the examples.

13. A multilayer coating or a process for producing same substantially as hereinbefore described with reference to the examples.